

WHAT IS CLAIMED IS:

- 1 1. A method for removing and recovering an ion from a solution
2 comprising:
 - 3 (a) contacting said solution with a solid ion extractant comprising a
4 recyclable activated ion coordinating agent to remove at least a portion of said ion from said
5 solution;
 - 6 (b) deactivating said ion coordinating agent;
 - 7 (c) dissolving said ion in a recovery solvent and removing said ion from
8 said solid ion extractant; and
 - 9 (d) recovering said ion from said recovery solvent.
- 1 2. The method of Claim 1, wherein said ion is an anion.
- 1 3. The method of Claim 1, wherein said ion is a perfluoroalkylsulfonate
2 or a perfluoroalkyl carboxylate.
- 1 4. The method of Claim 1, wherein said ion coordinating agent comprises
2 a lipophilic portion.
- 1 5. The method of Claim 1, wherein said active ion coordinating agent is
2 ionizable in an aqueous solution.
- 1 6. The method of Claim 1, wherein said step of removing said ion from
2 said solution comprises an ion-exchange process.
- 1 7. The method of Claim 1, wherein said ion coordinating agent is an
2 organometallic compound.
- 1 8. The method of Claim 7, wherein said ion coordinating agent is redox-
2 recyclable.
- 1 9. The method of Claim 8, wherein said ion coordinating agent is
2 oxidized prior to said step (a).
- 1 10. The method of Claim 9, wherein said oxidation step comprises an
2 electrochemical oxidation process.

1 11. The method of Claim 9, wherein said oxidation step comprises a
2 chemical oxidation process.

1 12. The method of Claim 8, wherein said deactivation step comprises
2 reducing said ion coordinating agent.

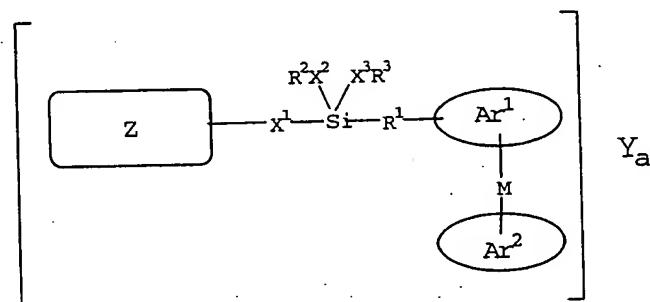
1 13. The method of Claim 12, wherein said reduction step comprises an
2 electrochemical reduction process.

1 14. The method of Claim 12, wherein said reduction step comprises a
2 chemical reduction process.

1 15. The method of Claim 14, wherein said chemical reduction process
2 comprises contacting said solid ion extractant with a deactivating solution.

1 16. The method of Claim 15, wherein said deactivating solution comprises
2 a compound selected from the group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$, Cr^{2+}
3 salt, V^{2+} salt and NaBH_4 .

1 17. The method of Claim 1, wherein said solid ion extractant is a
2 composition of the formula:



3 wherein
4 each of Ar^1 and Ar^2 is independently $\text{C}_4\text{-C}_{20}$ aryl;

5 M is a transition metal;

6 R^1 is $\text{C}_2\text{-C}_{20}$ alkylene;

7 each of X^1 , X^2 and X^3 is independently a bond, O, S, or NR^4 ;

8 each of R^2 , R^3 and R^4 is independently H, or $\text{C}_1\text{-C}_6$ alkyl;

9 Z is a solid support;

10 Y is an anion; and

12 a is 0 when said ion coordinating agent is deactivated, and
13 a is an integer from 1 to 3 when said ion coordinating agent is activated.

1 18. The method of Claim 17, wherein M is selected from the group
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 19. The method of Claim 17, wherein Ar¹ and Ar² are selected from the
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
3 optionally substituted.

1 20. The method of Claim 17, wherein each of X¹, X² and X³ is
2 independently a bond or O.

1 21. The method of Claim 17, wherein R² and R³ are C₁-C₆ alkyl.

1 22. The method of Claim 17, wherein said solid support is glass or a
2 polymeric resin.

1 23. The method of Claim 22, wherein said polymeric resin is selected from
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and
3 polyaromatic.

1 24. The method of Claim 17, wherein Y is selected from the group
2 consisting of nitrate, halide, HSO₄⁻, ClO₄⁻, ReO₄⁻, PF₆⁻, carboxylate and CF₃SO₃⁻.

1 25. The method of Claim 17, wherein a is 1 when said ion coordinating
2 agent is activated.

1 26. The method of Claim 1, wherein said solution is an aqueous solution.

1 27. The method of Claim 26, wherein the temperature of solution of said
2 step (a) is least about 24 °C.

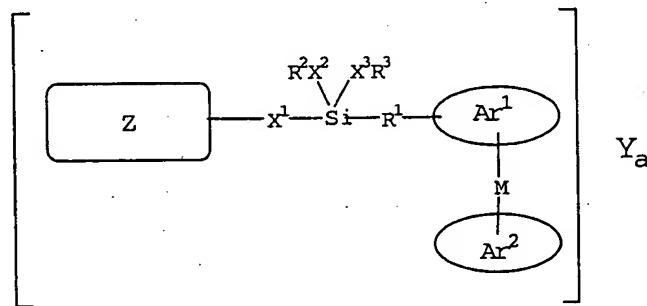
1 28. The method of Claim 1, wherein the temperature of said recovery
2 solution is at least about 85 °C.

1 29. The method of Claim 28, wherein said recovery step (d) comprises
2 reducing the temperature of said recovery solution to less than about 5 °C to precipitate said
3 ion.

1 30. The method of Claim 29, wherein said recovery step further comprises
2 separating said precipitated ion from said recovery solution.

1 31. The method of Claim 1, further comprising:
2 (e) re-activating said deactivated ion coordinating agent; and
3 (f) repeating said steps (a)-(e).

1 32. A method for removing and recovering an anion from an aqueous
2 solution comprising:
3 (a) contacting said solution with a solid ion extractant comprising an ion
4 coordinating agent to remove at least a portion of said anion from said aqueous solution,
5 wherein said solid ion extractant is a composition of the formula:



6 wherein

7 each of Ar^1 and Ar^2 is independently C₄-C₂₀ aryl;

8 M is a transition metal;

9 R^1 is C₂-C₂₀ alkylene;

10 each of X^1 , X^2 and X^3 is independently a bond, O, S, or NR⁴;

11 each of R^2 , R^3 and R^4 is independently H, or C₁-C₆ alkyl;

12 Z is a solid support;

13 Y is an anion; and

14 a is an integer from 1 to 3;

15 (b) reducing said ion coordinating agent in said solid ion extractant such

16 that a is 0;

1 33. The method of Claim 32, wherein said anion is a perfluoroalkyl
2 sulfonate or perfluoroalkyl carboxylate.

1 34. The method of Claim 32, wherein said step of removing said anion
2 from said aqueous solution comprises an ion-exchange process.

1 35. The method of Claim 32, wherein a in said step (a) is 1.

1 36. The method of Claim 32, wherein said ion coordinating agent is redox-
2 recyclable.

1 37. The method of Claim 36, further comprising a step of oxidizing said
2 ion coordinating agent from $a=0$ to $a=1$ prior to said step (a).

1 38. The method of Claim 37, wherein said oxidizing step comprises an
2 electrochemical oxidation process.

1 39. The method of Claim 37, wherein said oxidizing step comprises a
2 chemical oxidation process.

1 40. The method of Claim 36, wherein said deactivation step comprises
2 reducing said ion coordinating agent.

1 41. The method of Claim 40, wherein said reducing step comprises an
2 electrochemical reduction process.

1 42. The method of Claim 40, wherein said reducing step comprises a
2 chemical reduction process.

1 43. The method of Claim 42, wherein said chemical reduction process
2 comprises contacting said solid ion extractant with a deactivating solution.

1 44. The method of Claim 43, wherein said deactivating solution comprises
2 a compound selected from the group consisting of $\text{Na}_4\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{Na}_2\text{S}_2\text{O}_4$, Cr^{2+}
3 salt, V^{2+} salt and NaBH_4 .

1 45. The method of Claim 32, wherein M is selected from the group
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 46. The method of Claim 45, wherein Ar¹ and Ar² are selected from the
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
3 optionally substituted.

1 47. The method of Claim 46, wherein each of X¹, X² and X³ is
2 independently a bond or O.

1 48. The method of Claim 47, wherein R² and R³ are C₁-C₆ alkyl.

1 49. The method of Claim 48, wherein said solid support is glass or a
2 polymeric resin.

1 50. The method of Claim 49, wherein said polymeric resin is selected from
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and
3 polyaromatic.

1 51. The method of Claim 50, wherein Y is selected from the group
2 consisting of nitrate, halide, HSO₄⁻, ClO₄⁻, ReO₄⁻, PF₆⁻, carboxylate and CF₃SO₃⁻.

1 52. The method of Claim 32, wherein the temperature of said aqueous
2 solution of said step (a) is least about 24 °C.

1 53. The method of Claim 52, wherein the temperature of said recovery
2 solution is at least about 85 °C.

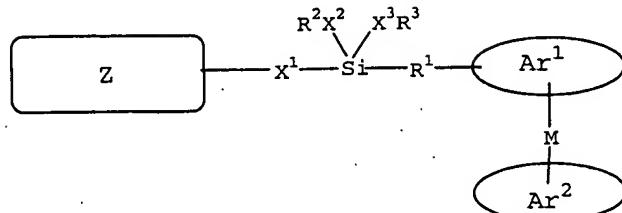
1 54. The method of Claim 53, wherein said recovery step (d) comprises
2 reducing the temperature of said recovery solution to less than about 5 °C to precipitate said
3 anion.

1 55. The method of Claim 54, wherein said recovery step further comprises
2 separating said precipitated ion from said recovery solution.

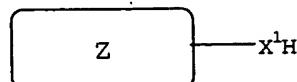
1 56. The method of Claim 32, further comprising:
2 (e) re-activating said deactivated ion coordinating agent; and

3 (f) repeating said steps (a)-(e).

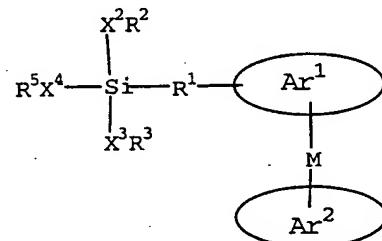
1 57. A process for producing a solid ion extractant composition of the
2 formula:



3
4 said process comprising contacting the solid support of the composition:
5



6 with an ion coordinating agent of the formula:
7



8 wherein

9 each of Ar^1 and Ar^2 is independently C_4-C_{20} aryl;

10 each of X^1 , X^2 , X^3 and X^4 is independently a bond, O, S, or NR^4 ;

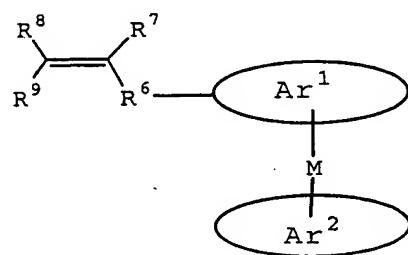
11 R^1 is C_2-C_{20} alkylene;

12 each of R^2 , R^3 , R^4 and R^5 is independently H, or C_1-C_6 alkyl;

13 M is a transition metal; and

14 Z is a solid support.

1 58. The process of Claim 57, further comprising the step of producing said
2 ion coordinating agent, wherein said ion coordinating agent producing step comprises
3 contacting an olefin of the formula:



4

5 with a silyl compound of the formula $\text{HSi}(\text{X}^2\text{R}^2)(\text{X}^3\text{R}^3)(\text{X}^4\text{R}^5)$ in the presence of a catalyst to
6 produce said ion coordinating agent,
7 wherein

8 R^6 is a bond or $\text{C}_1\text{-}\text{C}_{18}$ alkylene; and
9 each of R^7 , R^8 and R^9 is independently H or $\text{C}_1\text{-}\text{C}_6$ alkyl.

1 59. The method of Claim 58, wherein said catalyst is selected from the
2 group consisting of Karstedt's catalyst, Speier's catalyst, other silylplatinum complexes,
3 transition metal nanoclusters, dicobalt octacarbonyl, nickel tetracarbonyl, Wilkonsen's
4 catalyst, chromium hexacarbonyl, and zirconocenes.

1 60. The process of Claim 57, wherein M is selected from the group
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 61. The process of Claim 60, wherein Ar^1 and Ar^2 are selected from the
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
3 optionally substituted.

1 62. The process of Claim 61, wherein each of X^1 , X^2 and X^3 are
2 independently a bond or O.

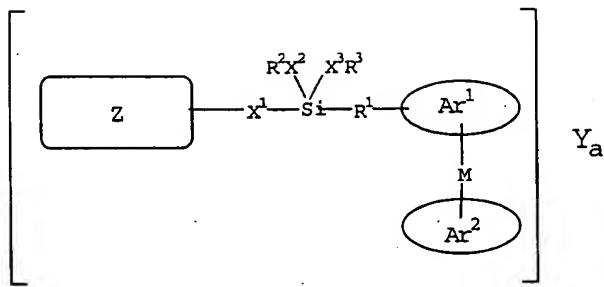
1 63. The process of Claim 62, wherein X^4 is O.

1 64. The process of Claim 63, wherein R^2 , R^3 and R^5 are $\text{C}_1\text{-}\text{C}_6$ alkyl.

1 65. The process of Claim 64, wherein said solid support is glass or a
2 polymeric resin.

1 66. The process of Claim 65, wherein said polymeric resin is selected from
2 the group consisting of acrylic ester, polyvinyl, polystyrene, polypyrrole, polyolefin, and
3 polyaromatic.

1 67. The process of Claim 57, further comprising oxidizing said solid ion
2 extractant to produce an activated solid ion extractant of the formula:



3

4 wherein

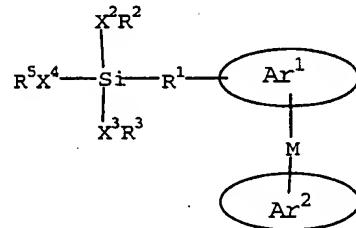
5 Y is an anion; and

6 a is an integer from 1 to 3.

1 68. The process of Claim 67, wherein a is 1.

1 69. The process of Claim 67, wherein Y is selected from the group
2 consisting of nitrate, halide, HSO_4^- , ClO_4^- , ReO_4^- , PF_6^- , carboxylate and CF_3SO_3^- .1 70. The process of Claim 67, wherein said oxidizing step comprises an
2 electrochemical oxidation process.1 71. The process of Claim 67, wherein said oxidizing step comprises a
2 chemical oxidation process.1 72. The process of Claim 71, wherein said chemical oxidation process
2 comprises contacting said solid ion extractant with a solution comprising an oxidant to
3 produce said activated solid ion extractant.1 73. The process of Claim 72, wherein said oxidant is selected from the
2 group consisting of $\text{Fe}(\text{NO}_3)_3$, AgNO_3 , FeCl_3 , AgF , NaOCl , $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ and $\text{Ce}(\text{SO}_4)_2$.

1 74. A compound of the formula:



2

3 wherein

4 each of Ar^1 and Ar^2 is independently $\text{C}_{4-\text{C}_{20}}$ aryl;5 each of X^1 , X^2 , X^3 and X^4 is independently a bond, O, S, or NR^4 ;

6 R¹ is C₂-C₂₀ alkylene;
7 each of R², R³, R⁴ and R⁵ is independently H, or C₁-C₆ alkyl; and
8 M is a transition metal.

1 75. The compound of Claim 74, wherein M is selected from the group
2 consisting of Fe, Ru, Mn, Co, Ni, Cr, Os, Rh and Ir.

1 76. The compound of Claim 74, wherein Ar¹ and Ar² are selected from the
2 group consisting of cyclopentadienyl, dicarbollide and phenyl, each of which can be
3 optionally substituted.

1 77. The compound of Claim 74, wherein each of X¹, X², X³ and X⁴ is
2 independently a bond or O.

1 78. The compound of Claim 74, wherein R² and R³ are C₁-C₆ alkyl.